PB82-127945

Field Disposal of Methyl Parathion Using Acidified Powered Zinc

(U.S.) Health Effects Research Lab.
Wenatchee, WA

Sep 81

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3.
EPA-600/J-80-012	JOURNAL ARTICULE	PB82-127945

4. TITLE AND SUBTITLE	5. REPORT DATE
Field Disposal of Methyl Parathion Using Acidified Powered Zinc	September 1981
	6. PERFORMING ORGANIZATION CODE 308090

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Larry C. Butler, Donald C. Staiff, G. Wayne Sovocool and James E. Davis	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Wenatchee Pesticides Branch/ETD Health Effects Research Lab US Environmental Protection Agency Wenatchee, WA 98801	ACAE1A
	11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Office of Research and Development (RTP,NC) Health Effects Research Laboratory US Environmental Protection Agency Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE EPA-600/11

15. SUPPLEMENTARY NOTES

Published In: Journal of Environmental Health Sciences B16(1): 49-58, 1981

16. ABSTRACT

The degradation of methyl parathion in soil with various amounts of acidified powdered zinc under field conditions was studied. Treatment was progressively more effective with increasing amounts of zinc. Disappearance of parent compound was followed for 2 1/2 years. The expected conversion product aminomethyl parathion and its N-methyl derivative were formed. In addition, N,N-dimethylamino, and the azo and azoxy condensation products were characterized by high resolution mass spectrometry. Aminomethyl parathion was shown to be identical to an authentic standard. The other specific positional isomers were considered likely, but were not proven by mass spectrometry. Structure elucidation was made with high resolution mass spectrometry, using the direct insertion probe, and with gas chromatography/low resolution mass spectrometry.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA-600/J-80-012
Journal Article

J. ENVIRON. SCI. HEALTH, B16(1), 49-58 (1981)

FIELD DISPOSAL OF METHYL PARATHION USING ACIDIFIED POWDERED ZINC

KEY WORDS: Methyl parathion, disposal, insecticide persistence, zinc, soil

Larry C. Butler, Donald C. Staiff, G. Wayne Sovocool*, and James E. Davis

Wenatchee Pesticides Research Branch
Environmental Toxicology Division
Health Effects Research Laboratory
U. S. Environmental Protection Agency
Wenatchee, Washington 98801

*Chemistry Branch, Environmental Toxicology Division
Health Effects Research Laboratory
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

ABSTRACT

The degradation of methyl parathion in soil with various amounts of acidified powdered zinc under field conditions was studied. Treatment was progressively more effective with increasing amounts of zinc. Disappearance of parent compound was followed for 2 1/2 years. The expected conversion product aminomethyl parathion and its N-methyl derivative were formed. In addition, N,N-dimethylamino, and the azo and azoxy condensation products were characterized by high resolution mass spectrometry.

Aminomethyl parathion was shown to be identical to an authentic standard. The other specific positional isomers were considered likely, but were not proven by mass spectrometry. Structure elucidation was made with high resolution mass spectrometry, using the direct insertion probe, and with gas chromatography/low resolution mass spectrometry.

INTRODUCTION

The pesticide, methyl parathion (O,O-dimethyl O-p-nitrophenyl phosphorothioate) is one of the highly toxic organophosphorus pesticides that has found increased usage in recent years, especially as a substitute for DDT on certain crops. If our experience with other high usage pesticides can serve as a guide, increased usage should lead to an increase in the amount of outdated or unwanted methyl parathion on farms. In view of the fact that disposal of small quantities of pesticides by open field burial may be permitted,[1] we felt there was a need for additional research to develop practical and economical means for degrading unused methyl parathion in an effort to reduce the hazard to human health and to minimize the environmental impact where such disposal may be allowed.

Earlier studies by this laboratory[2] indicated that the addition of powdered zinc in an acidic medium to DDT during disposal by burial showed some promise as a practical means of degrading small quantities of the pesticide to environmentally less objectionable compounds. Shih and Dal Porto[3] reviewed the literature

concerning laboratory reactions that might be applicable to disposal of methyl parathion. They concluded that oxidation or hydrolysis were not desirable because these reactions result in the formation, respectively, of methyl paraoxon (O,O-dimethyl O-p-nitrophenyl phosphate) which is more toxic than methyl parathion, and p-nitrophenol, which is nearly as toxic as methyl parathion. They also concluded that reduction of methyl parathion with acid and zinc to aminomethyl parathion (O,O-dimethyl O-p-aminophenyl phosphorothioate) warranted further investigation as a disposal procedure.

This reaction would be analogous to the reduction employed by Averell and Norris[4] for the analysis of parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate). The purpose of the present study was to determine if, under field conditions, this reaction would accelerate degradation of methyl parathion to its less toxic p-aminophenyl derivative and/or produce breakdown products less toxic and more environmentally acceptable than the parent compound. Test plots were monitored to determine if there were further changes of breakdown products during an extended period of time.

MATERIALS AND METHODS

The experiment involved mixing of soil, emulsifiable concentrate (E.C.) methyl parathion, powdered zinc, dilute acetic acid and solvent in an effort to hasten pesticide degradation. Test plots in the field were formed by placing hollow concrete blocks in the soil deep enough to allow the upper surface to be covered

with approximately 10 cm of soil. The concrete blocks acted as buried containers delineating the areas where samples were taken. From 1 1/2 to 2 L of loosely packed soil was placed in each block cavity and different amounts of powdered zinc mesh No. 50 (No. 50 zinc dust, American Smelting and Refining Co. - 97% passes through a 325 sieve) was added and mixed well into the soil. The amounts of zinc added were 1.5 mmoles, 7.5 mmoles, 15.0 mmoles, or 30.0 mmoles, per 4 mmoles of methyl parathion active ingredient, resulting in molar ratios of Zn to methyl parathion of 0.3, 1.9, 3.8, and 7.7. Each level of zinc was replicated four times. After addition of the zinc, the following were added in this order with stirring: (1) 473 ml of 45.1% active ingredient methyl parathion emulsifiable concentrate pesticide formulation; (2) 400 ml of reagent grade acetone; (3) 250 ml of 10% acetic acid/water solution. After waiting one hour to allow the reaction to subside the initial samples for analysis were taken. The blocks were then covered with approximately 10 cm of soil. Controls were also replicated four times.

Untreated controls contained the same amount of emulsifiable concentrate methyl parathion as in the test blocks but no zinc, acid, or acetone was added. A set of "blank" controls contained soil mixed with zinc, acid, and acetone but no methyl parathion. All test blocks were left in place for the duration of the experiment.

Experimental plots were subjected to the natural elements such as rainfall (average approximately 25 cm per year), sunlight

(over 275 days per year), and relatively high maximum temperatures (over 32°C for an average of 14 days each summer). The plots were covered with snow for approximately two months each year. Soil used in the concrete block containers was classified as sandy loam containing 10.2 to 11.2% clay, 29 to 34.2% silt, 54.6 to 60.8% sand, and 2.5 to 3.5% organic matter. The soil pH ranged from 6.7 to 7.4 with a mean of 7.1.

Sampling at the 1 and 2 1/2 year periods was accomplished by carefully removing the soil covering and placing it in a clean container. The zone of soil containing the reacted pesticide was delineated by its firmness in relation to the soft and more loosely packed soil on top. Samples were taken with clean, sharp cork borers, or with spatulas if the soil samples were too hard for the cork borer. All soil sampling equipment was either cleaned between samples or clean new tools were employed. Sampling was performed in a clockwise manner within each block in order to avoid taking soil from a previously sampled location where dilution by nonrepresentative top soil may have occurred. After sampling was accomplished, the top soil that had been removed was placed back into the crater in the concrete block.

The samples were air dried to a constant weight and final drying was accomplished by grinding the soil-pesticide mixture in a mortar with anhydrous sodium sulfate. They were then Soxhlet extracted with gas chromatographic grade benzene and stored in amber bottles pending analysis.

Methyl parathion residues were analyzed using a Tracor flame photometric detector operated in the phosphorus mode. A glass column, 1.83 m x 3.7 mm, packed with 1.5% OV-17/1.95% OV-210 on 80/100 mesh Gas Chrom Q was used with a nitrogen carrier flow rate of 55 ml/min and a temperature of 180°C.

Sample extracts from the reduction of methyl parathion with 30.0 mmole acidified powdered zinc, initial and one year periods, were analyzed by gas chromatography/mass spectrometry. A Hewlett Packard 5930A mass spectrometer, equipped with a Hewlett Packard 5933A data system and a 5700A gas chromatograph, was employed. The 1.83 m x 2 mm gas chromatographic column of 1.5% OV-17/1.95% OV-?10 on 80/100 mesh Gas Chrom Q was programmed from 150°C (2 min) to 230°C at 8°C/min.

Exact mass measurements were obtained with a Varian MAT 311 high resolution mass spectrometer. The following settings were employed: 3 KV acceleration voltage, 70 eV electron energy, 2 mA electron current, 7000-8000 resolution and 220°C ion source temperature. Samples were run by inserting the mixture directly into the ion source of the mass spectrometer and heating from 40 to 250°C. Exact mass measurements were made by manual peak matching against a perfluorokerosene internal mass standard.

RESULTS AND DISCUSSION

As can be seen in Table 1, the acidified powdered zinc treatment at burial was effective in degrading methyl parathion. The treatment was more effective with increasing amounts of zinc.

TABLE 1

Degradation of Methyl Parathion in Soil Plots with Acidified Powdered Zinc, Acetone, and 10% Acetic Acid[a]

Treatment[b]	Methyl parathion recovery (μg/g of soil) at different times after treatment.[c]		
	Initial	1 Year	2 Years
Blank control, 7.5 mmoles zinc	0	0	0
No zinc	2,950 ± 192	2,060 ± 91	3,700 ± 592
1.5 mmoles zinc	3,570 ± 406	1,980 ± 494	2,570 ± 98
7.5 mmoles zinc	2,430 ± 507	442 ± 121	60.8 ± 6.5
15.0 mmoles zinc	1,480 ± 525	13.8 ± 2.5	12.2 ± 2.5
30.0 mmoles zinc	30.7 ± 10.8	8.5 ± 3.3	5.7 ± 0.9

[a]Experimental conditions are given under methods.

[b]The blank control contained no methyl parathion. All of the other treatments contained 4.0 mmoles of methyl parathion.

[c]Mean ± standard error for 4 replicates.

The greatest degradation was observed with the highest amounts of zinc after 2 1/2 years of burial. Apparent increases at 2 1/2 years in the methyl parathion content of soil samples obtained from the plots containing no zinc or 1.5 mmoles of zinc reflect the difficulty encountered in obtaining homogeneous samples from experimental plots used to simulate field conditions.

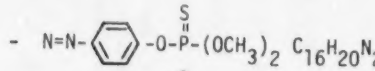
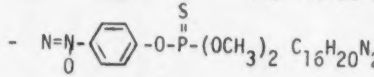
It was not practicable to identify all the reaction products in the extracts from all of the powdered zinc-acetic acid reductions of methyl parathion. However, analysis by gas chromatography/mass spectrometry of extracts from the 30.0 mmole acidified

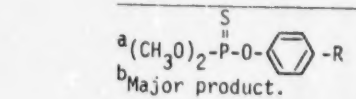
zinc reduction, initial and one year periods, confirmed the formation of the expected conversion product, aminomethyl parathion, and disclosed the formation of at least four additional products formed by aminomethylation and azo or azoxy coupling. These additional products probably were N-methylaminomethyl parathion (O-[p-(methylamino)phenyl]O,O-dimethyl phosphorothioate), N,N-dimethylaminomethyl parathion (O-[p-(dimethylamino)phenyl]O,O-dimethyl phosphorothioate), p,p'-bis[(dimethoxyphosphinothioyl)oxy]azobenzene, and p,p'-bis[(dimethoxyphosphinothioyl)oxy]azoxybenzene. The additional products were tentatively assigned structures consistent with exact mass measurements and reasonable chemical transformations[5] (see Table 2). Final identification and quantitation of these products would require independent synthesis of each compound with further chemical and instrumental analysis.

The oxidative instability of primary aromatic amines[6] partly prompted the consideration that reduction of the nitro group of methyl parathion should significantly hasten degradation of the reaction products as well as the parent compound. Since it is known that aminoparathion is much less toxic to animals than parathion,[7] then by analogy, aminomethyl parathion may be less toxic than methyl parathion. Toxicity data could not be found for the four other products formed during the powdered zinc-acetic acid reduction of methyl parathion. Before degradation of methyl parathion by this method could be recommended as a suitable field disposal procedure, the acute and chronic toxicities of the unexpected conversion products should be investigated.

TABLE 2

Summary of Exact Mass Data from High Resolution Mass Spectrometry

Compound[a]	-R	Assigned Composition	Exact Mass Exp.	Exact Mass Ther.	Error
Methyl parathion	$-NO_2$	$C_8H_{10}O_5NPS$	263.0004	263.0018	5.3
Aminomethyl parathion[b]	$-NH_2$	$C_8H_{12}O_3NPS$	233.0273	233.0276	1.3
Methylaminomethyl parathion[c]	$-NHCH_3$	$C_9H_{14}O_3NPS$	247.0430	247.0432	1.8
Dimethylaminomethyl parathion[c]	$-N(CH_3)_2$	$C_{10}H_{16}O_3NPS$	261.0589	261.0589	0.0
Azo product[c]		$C_{16}H_{20}N_2O_6P_2S_2$	462.0220	462.0238	3.8
Azoxy product[c]		$C_{16}H_{20}N_2O_7P_2S_2$	478.0177	478.0187	2.1

[a] 

[b] Major product.

[c] Minor product.

This study is a particularly good example of the need for actual field trials for disposal systems which appear very promising on a theoretical or even small scale laboratory basis, but which may result in completely unexpected products when used under field conditions.

ACKNOWLEDGEMENTS

The authors are grateful to Dorothy Fillman, Robert L. Harless, Louis E. Feige, and Stephen D. Soileau for technical assistance.

REFERENCES

1. Federal Register, 39, 15236 (May 1, 1974).

2. Staiff, D. C., L. C. Butler and J. E. Davis, J. Environ. Sci. Health B12, 1 (1977).

3. Shih, C. C. and D. F. Dal Porto, Handbook for Pesticide Disposal by Common Chemical Methods, TRW Systems Group, PB-252 864, U. S. Department of Commerce, National Technical Information Service, Springfield, Virginia, 103 (1975).

4. Averell, P. R. and M. V. Norris, Anal. Chem. 20, 753 (1948).

5. Cram, D. J. and G. S. Hammond, Organic Chemistry, 2nd ed., McGraw-Hill, New York, N. Y., 560-561 (1964).

6. Fieser, L. F. and M. Fieser, Advanced Organic Chemistry, Reinhold, New York, N.Y., 716 (1961).

7. Ahmed, M. K., J. E. Casida, and R. E. Nichols, J. Agr. Food Chem. 6, 740 (1958).

Received: June 19, 1980.